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Electronic Supplementary Information

Inorganic-Organic Hybrid Zinc Phosphites with Fluorescence/ Phosphorescence Dual Emission Performances

Ai-Yun Ni, Ying Mu, Jie Pan, Song-De Han, Jin-Hua Li and Guo-Ming Wang,*

College of Chemistry and Chemical Engineering, Qingdao University, Shandong 266071, P. R. China. *E-mail: gmwang_pub@163.com

Synthesis of QDU-6a and QDU-6b

All chemicals were reagent grade and used as purchased without further purification. A mixture of ZnO (0.04 g, 0.49 mmol), H_3PO_3 (0.24 g, 2.93 mmol), tib (0.02 g, 0.07 mmol), DMF (*N,N*-dimethylformamide) or DMA (*N,N*-dimethylacetamide) (0.5 ml) and H_2O (1.5 ml) was sealed in a Teflon-lined autoclave (20 mL) and heated to 145°C for 1 day then slowly cooled to 30°C in 12 h. CHN analyses confirmed their stoichiometry. Anal. calcd for $C_{33}H_{47}N_{13}O_{24}P_6Zn_6$ (QDU-6a): C, 24.96; H, 2.96; N, 11.47 wt%. Found: C, 24.92; H, 3.02; N, 11.40 wt%. Anal. calcd for $C_{34}H_{49}N_{13}O_{24}P_6Zn_6$ (QDU-6b): C, 25.49; H, 3.06 ; N, 11.37 wt%. Found: C, 25. 40; H, 2.98; N, 11.26 wt%.

Characterization

Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert-MPD diffractometer by using Cu-Kα1 radiation (λ = 1.54076 Å). Thermogravimetric analysis was performed with temperature ranging from 30 to 800 °C on a NETZSCH STA 449 F5 instrument. Elemental analysis (EA for CHN) was measured on a Perkin-Elmer 240C analyzer. The prompt and delayed photoluminescence spectra were measured on a HORIBA Scientific Fluoromax-4P spectrophotometer. The time-resolved decay spectra, temperature dependent photoluminescence spectra and absolute luminescence quantum yield were measured on an Edinburgh FLSP 920 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900), a microsecond flash-lamp (uF2), a picosecond pulsed diode laser (EPL-280), a closed cycle cryostate (CS202*I-DMX-1SS, Advanced Research Systems) and an integrating sphere, respectively. The fluorescent microscopy images were taken by a Nikon ECLIPSE T*i* excited at UV light and collected through band-pass filter of 450 nm wavelengths.

Crystallography

The crystallographic data of QDU-6a and QDU-6b was collected on a XtaLAB-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The structures were solved by the SHELX-2016 software. To make the crystallography data of DMF molecules more reasonable, some instruments (dfix, simu, isor, delu, flat) were used. Detailed crystallographic data for QDU-6a and QDU-6b is summarized in Table S1 and Table S3 and the selected bond lengths and angles are given in Table S2 and Table S4. Full crystallographic data for QDU-6a and QDU-6b has been deposited with the CCDC (1851924 and 1851925), which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk). Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program

available free of charge *via* the Internet at http://www.iucr.org. The solvent accessible volume is estimated by the PLATON program and the point symbol for the net is calculated by the TOPOS program.[1,2]

References

1. A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
2. V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193.

Table S1. Crystal data and structure refinement parameters for **QDU-6a**

	QDU-6a	
Formula	$C_{33}H_{47}N_{13}O_{24}P_6Zn_6$	
*M*r (g mol^{-1})	1587.88	
Space group	*P2$_1$/n*	
Crystal system	monclinic	
a (Å)	10.1876(8)	
b (Å)	26.5744(19)	
c (Å)	20.1478(16)	
α (°)	90	
β (°)	92.089(7)	
γ (°)	90	
V (Å^3)	5451.0(7)	
Z	4	
F(000)	3192	
Dc (gcm^{-3})	1.935	
μ (mm^{-1})	2.867	
R_{int}	0.0561	
limiting indices	-12≤ h ≤6	
	-28≤ k ≤31	
	-23≤ l ≤21	
Collected reflections	19804	
Unique reflections	9592	
GOF on F^2	1.059	
R_1, wR_2 [I>2σ(I)]	0.0550	0.1327
R_1, wR_2 [all data]	0.0965	0.1579

Table S2. Selected bond lengths (Å) and angles (°) for **QDU-6a**

O(1)-P(1)	1.513(4)	Zn(3)-O(5)	1.949(5)
O(2)-P(1)	1.503(5)	Zn(3)-N(9)#1	1.999(5)
O(3)-P(1)	1.523(5)	Zn(4)-O(10)	1.895(5)
O(4)-P(2)	1.515(5)	Zn(4)-O(14)	1.919(5)
O(5)-P(2)	1.497(5)	Zn(4)-O(9)	1.942(4)
O(6)-P(2)	1.517(5)	Zn(4)-N(5)#2	1.991(6)
O(7)-P(3)	1.506(5)	Zn(5)-O(13)	1.897(5)
O(8)-P(3)	1.485(5)	Zn(5)-O(16)	1.905(5)
O(9)-P(3)	1.507(5)	Zn(5)-O(12)	1.940(5)
O(10)-P(4)	1.486(5)	Zn(5)-N(3)#3	2.012(5)
O(11)-P(4)	1.488(5)	Zn(6)-O(18)#4	1.903(4)
O(12)-P(4)	1.522(5)	Zn(6)-O(15)	1.903(5)
O(13)-P(5)	1.498(5)	Zn(6)-O(17)	1.945(4)
O(14)-P(5)	1.496(5)	Zn(6)-N(11)#5	2.029(5)
O(15)-P(5)	1.493(5)	Zn(1)-O(1)#1	1.916(4)
O(16)-P(6)	1.508(5)	Zn(1)-O(3)	1.927(5)
O(17)-P(6)	1.517(4)	Zn(1)-O(6)	1.931(4)
O(18)-P(6)	1.509(4)	Zn(1)-N(1)	2.023(6)
Zn(2)-O(7)	1.926(5)	O(1)-Zn(1)#1	1.916(4)
Zn(2)-O(2)	1.932(5)	O(18)-Zn(6)#4	1.903(4)
Zn(2)-O(4)	1.934(4)	N(9)-Zn(3)#1	1.999(5)
Zn(2)-N(7)	2.009(5)	N(11)-Zn(6)#6	2.029(5)
Zn(3)-O(8)	1.900(5)	N(3)-Zn(5)#7	2.012(5)
Zn(3)-O(11)	1.907(5)	N(5)-Zn(4)#8	1.991(6)
O(2)-P(1)-O(1)	111.0(3)	O(13)-Zn(5)-O(16)	113.3(3)
O(2)-P(1)-O(3)	113.9(3)	O(13)-Zn(5)-O(12)	114.4(2)
O(1)-P(1)-O(3)	112.5(3)	O(16)-Zn(5)-O(12)	110.0(2)
O(5)-P(2)-O(4)	114.2(3)	O(13)-Zn(5)-N(3)#3	111.4(2)
O(5)-P(2)-O(6)	111.6(3)	O(16)-Zn(5)-N(3)#3	102.5(2)
O(4)-P(2)-O(6)	113.6(3)	O(12)-Zn(5)-N(3)#3	102.5(2)
O(8)-P(3)-O(7)	111.3(3)	O(18)#4-Zn(6)-O(15)	102.5(2)
O(8)-P(3)-O(9)	114.1(3)	O(18)#4-Zn(6)-O(17)	114.6(2)
O(7)-P(3)-O(9)	113.2(3)	O(15)-Zn(6)-O(17)	109.5(2)
O(11)-P(4)-O(10)	116.3(3)	O(18)#4-Zn(6)-N(11)#5	109.8(2)
O(11)-P(4)-O(12)	112.1(3)	O(15)-Zn(6)-N(11)#5	105.1(2)
O(10)-P(4)-O(12)	112.4(3)	O(17)-Zn(6)-N(11)#5	103.7(2)
O(15)-P(5)-O(14)	112.9(4)	O(1)#1-Zn(1)-O(3)	112.4(2)
O(15)-P(5)-O(13)	112.9(3)	O(1)#1-Zn(1)-O(6)	110.0(2)
O(14)-P(5)-O(13)	113.9(3)	O(3)-Zn(1)-O(6)	113.0(2)
O(16)-P(6)-O(18)	110.8(3)	O(1)#1-Zn(1)-N(1)	104.5(2)

O(16)-P(6)-O(17)	112.2(3)	O(3)-Zn(1)-N(1)	108.3(2)
O(18)-P(6)-O(17)	113.3(3)	O(6)-Zn(1)-N(1)	108.2(2)
O(7)-Zn(2)-O(2)	114.4(2)	P(1)-O(1)-Zn(1)#1	128.1(3)
O(7)-Zn(2)-O(4	113.0(2)	P(1)-O(2)-Zn(2)	143.6(3)
O(2)-Zn(2)-O(4)	113.2(2)	P(1)-O(3)-Zn(1)	128.3(3)
O(7)-Zn(2)-N(7)	104.7(2)	P(2)-O(4)-Zn(2)	127.2(3)
O(2)-Zn(2)-N(7)	100.2(2)	P(2)-O(5)-Zn(3)	143.7(3)
O(4)-Zn(2)-N(7)	110.2(2)	P(2)-O(6)-Zn(1)	133.8(3)
O(8)-Zn(3)-O(11)	119.8(3)	P(3)-O(7)-Zn(2)	121.2(3)
O(8)-Zn(3)-O(5)	113.7(2)	P(3)-O(8)-Zn(3)	146.7(4)
O(11)-Zn(3)-O(5)	114.7(3)	P(3)-O(9)-Zn(4)	129.5(3)
O(8)-Zn(3)-N(9)#1	104.4(2)	P(4)-O(10)-Zn(4)	152.3(4)
O(11)-Zn(3)-N(9)#1	99.4(2)	P(4)-O(11)-Zn(3)	136.9(4)
O(5)-Zn(3)-N(9)#1	100.9(2)	P(4)-O(12)-Zn(5)	117.8(3)
O(10)-Zn(4)-O(14)	114.8(2)	P(5)-O(13)-Zn(5)	137.2(3)
O(10)-Zn(4)-O(9)	116.6(2)	P(5)-O(14)-Zn(4)	137.6(3)
O(14)-Zn(4)-O(9)	111.7(2)	P(5)-O(15)-Zn(6)	142.3(4)
O(10)-Zn(4)-N(5)#2	104.0(3)	P(6)-O(16)-Zn(5)	149.3(3)
O(14)-Zn(4)-N(5)#2	101.9(3)	P(6)-O(17)-Zn(6)	123.6(3)
O(9)-Zn(4)-N(5)#2	105.9(2)	P(6)-O(18)-Zn(6)#4	125.4(3)

Symmetry codes: #1: -x+2, -y+2, -z; #2: x-1/2, -y+3/2, z+1/2; #3: -x+7/2, y-1/2, -z-1/2; #4: -x+3, -y+1, -z; #5: -x+3/2, y-1/2, -z+1/2; #6: -x+3/2, y+1/2, -z+1/2; #7: -x+7/2, y+1/2, -z-1/2; #8: x+1/2, -y+3/2, z-1/2.

Table S3. Crystal data and structure refinement parameters for **QDU-6b**

	QDU-6b	
Formula	$C_{34}H_{49}N_{13}O_{24}P_6Zn_6$	
*M*r (g mol^{-1})	1601.90	
Space group	*P2$_1$/n*	
Crystal system	monclinic	
a (Å)	10.1955(8)	
b (Å)	26.678(2)	
c (Å)	20.1328(15)	
α (°)	90	
β (°)	92.010(7)	
γ (°)	90	
V (Å^3)	5472.6(7)	
Z	4	
F(000)	3224	
Dc (gcm^{-3})	1.944	
μ (mm^{-1})	2.856	
R_{int}	0.0519	
limiting indices	-12≤ h ≤10	
	-31≤ k ≤23	
	-16≤ l ≤23	
Collected reflections	20617	
Unique reflections	9622	
GOF on F^2	1.036	
R_1, wR_2 [I>2σ(I)]	0.0532	0.1318
R_1, wR_2 [all data]	0.0951	0.1516

Table S4. Selected bond lengths (Å) and angles (°) for **QDU-6b**

O(1)-P(1)	1.508(4)	O(10)-Zn(3)	1.903(5)
O(2)-P(1)	1.515(5)	O(11)-Zn(4)	1.908(5)
O(3)-P(1)	1.523(4)	O(12)-Zn(5)	1.939(5)
O(4)-P(2)	1.520(5)	O(13)-Zn(4)	1.913(5)
O(5)-P(2)	1.502(5)	O(14)-Zn(6)	1.919(5)
O(6)-P(2)	1.508(5)	O(15)-Zn(5)	1.895(4)
O(7)-P(3)	1.510(5)	O(16)-Zn(5)	1.928(5)
O(8)-P(3)	1.476(5)	O(17)-Zn(6)	1.950(4)
O(9)-P(3)	1.504(5)	O(18)-Zn(6)#5	1.905(4)
O(10)-P(4)	1.489(5)	Zn(1)-O(3)#4	1.924(4)
O(11)-P(4)	1.480(5)	Zn(1)-O(6)#4	1.934(5)
O(12)-P(4)	1.535(5)	Zn(2)-N(11)#4	1.990(6)
O(13)-P(5)	1.500(5)	Zn(4)-N(3)#6	1.991(6)
O(14)-P(5)	1.483(5)	Zn(5)-N(5)#7	2.012(5)
O(15)-P(5)	1.499(5)	Zn(6)-O(18)#5	1.905(4)
O(16)-P(6)	1.496(5)	Zn(6)-N(9)#8	2.034(5)
O(17)-P(6)	1.512(4)	N(1)-Zn(1)	2.021(5)
O(18)-P(6)	1.505(4)	N(3)-Zn(4)#1	1.991(6)
O(3)-Zn(1)#4	1.924(4)	N(5)-Zn(5)#2	2.012(5)
O(4)-Zn(2)	1.926(4)	N(7)-Zn(3)	1.994(6)
O(5)-Zn(3)	1.941(5)	N(9)-Zn(6)#3	2.034(5)
O(6)-Zn(1)#4	1.934(5)	N(11)-Zn(2)#4	1.990(6)
O(7)-Zn(2)	1.924(5)	O(1)-Zn(1)	1.916(4)
O(8)-Zn(3)	1.908(5)	O(2)-Zn(2)	1.928(5)
O(9)-Zn(4)	1.947(5)		
P(1)-O(1)-Zn(1)	128.2(3)	O(1)-Zn(1)-O(3)#4	112.59(19)
P(1)-O(2)-Zn(2)	144.1(3)	O(1)-Zn(1)-O(6)#4	109.8(2)
P(1)-O(3)-Zn(1)#4	128.3(3)	O(3)#4-Zn(1)-O(6)#4	112.4(2)
P(2)-O(4)-Zn(2)	126.6(3)	O(1)-Zn(1)-N(1)	105.2(2)
P(2)-O(5)-Zn(3)	144.3(3)	O(3)#4-Zn(1)-N(1)	107.8(2)
P(2)-O(6)-Zn(1)#4	135.0(3)	O(6)#4-Zn(1)-N(1)	108.7(2)
P(3)-O(7)-Zn(2)	121.3(3)	O(7)-Zn(2)-O(4)	112.7(2)
P(3)-O(8)-Zn(3)	146.1(4)	O(7)-Zn(2)-O(2)	115.1(2)
P(3)-O(9)-Zn(4)	129.4(3)	O(4)-Zn(2)-O(2)	113.1(2)
P(4)-O(10)-Zn(3)	137.5(4)	O(4)-Zn(2)-N(11)#4	109.3(2)
P(4)-O(11)-Zn(4)	151.1(4)	O(2)-Zn(2)-N(11)#4	100.5(2)
P(4)-O(12)-Zn(5)	117.7(3)	O(10)-Zn(3)-O(8)	119.1(2)
P(5)-O(13)-Zn(4)	137.8(3)	O(10)-Zn(3)-O(5)	114.7(3)
P(5)-O(14)-Zn(6)	141.8(3)	O(8)-Zn(3)-O(5)	114.1(2)
P(5)-O(15)-Zn(5)	137.2(3)	O(10)-Zn(3)-N(7)	100.3(2)

P(6)-O(16)-Zn(5)	148.5(3)	O(10)-Zn(3)-N(7)	103.8(2)
P(6)-O(17)-Zn(6)	123.5(3)	O(5)-Zn(3)-N(7)	100.9(2)
P(6)-O(18)-Zn(6)#5	125.8(3)	O(11)-Zn(4)-O(13)	114.6(2)
O(1)-P(1)-O(2)	111.5(3)	O(11)-Zn(4)-O(9)	117.2(2)
O(1)-P(1)-O(3)	112.1(3)	O(13)-Zn(4)-O(9)	112.3(2)
O(2)-P(1)-O(3)	113.3(3)	O(11)-Zn(4)-N(3)#6	103.4(3)
O(5)-P(2)-O(6)	111.2(3)	O(13)-Zn(4)-N(3)#6	101.7(3)
O(5)-P(2)-O(4)	114.1(3)	O(9)-Zn(4)-N(3)#6	105.5(2)
O(6)-P(2)-O(4)	113.1(3)	O(15)-Zn(5)-O(16)	115.0(2)
O(8)-P(3)-O(9)	114.1(3)	O(15)-Zn(5)-O(12)	113.3(3)
O(8)-P(3)-O(7)	111.9(3)	O(16)-Zn(5)-O(12)	110.8(2)
O(9)-P(3)-O(7)	112.8(3)	O(15)-Zn(5)-N(5)#7	111.6(2)
O(11)-P(4)-O(10)	116.6(4)	O(16)-Zn(5)-N(5)#7	102.2(2)
O(11)-P(4)-O(12)	112.6(3)	O(12)-Zn(5)-N(5)#7	102.6(2)
O(10)-P(4)-O(12)	112.4(3)	O(18)#5-Zn(6)-O(14)	113.2(3)
O(14)-P(5)-O(15)	113.7(3)	O(18)#5-Zn(6)-O(17)	114.42(19)
O(14)-P(5)-O(13)	112.8(4)	O(14)-Zn(6)-O(17)	110.0(2)
O(15)-P(5)-O(13)	113.4(3)	O(18)#5-Zn(6)-N(9)#8	109.4(2)
O(16)-P(6)-O(18)	110.0(3)	O(14)-Zn(6)-N(9)#8	105.6(2)
O(16)-P(6)-O(17)	112.6(3)	O(17)-Zn(6)-N(9)#8	103.5(2)
O(18)-P(6)-O(17)	113.2(3)		

Symmetry codes: #1: -x+1/2, y+1/2, -z+1/2; #2: x-3/2, -y+3/2, z+1/2; #3: x+1/2, -y+3/2, z-1/2; #4: -x+1, -y+2, -z; #5: -x+2, -y+1, -z; #6: -x+1/2, y-1/2, -z+1/2; #7: x+3/2, -y+3/2, z-1/2; #8: x-1/2, -y+3/2, z+1/2.

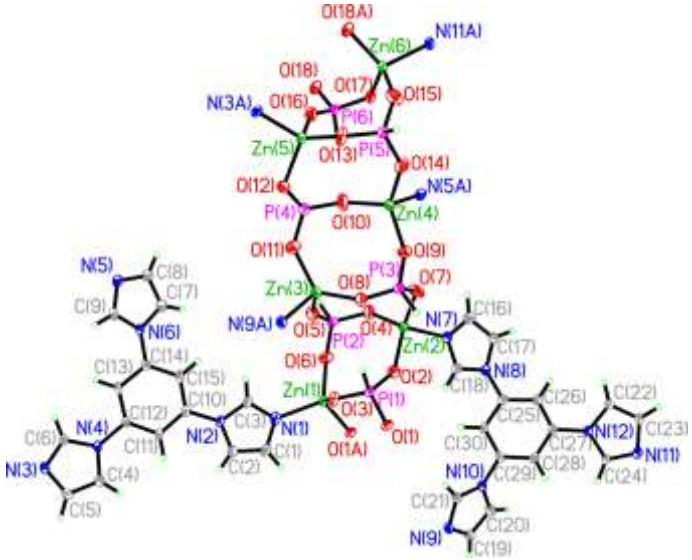

Fig. S1. ORTEP view of the coordination of the zinc and phosphorus atoms in the asymmetric unit of QDU-6a with 30% thermal ellipsoids.

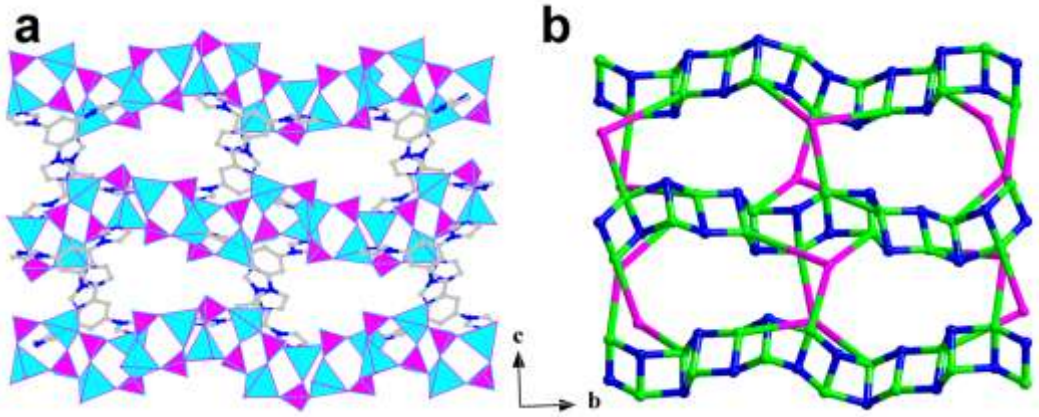

Fig. S2. (a) View of the 3D hybrid framework along the [100] direction; (b) The (3,4)-connected topological net of QDU-6a.

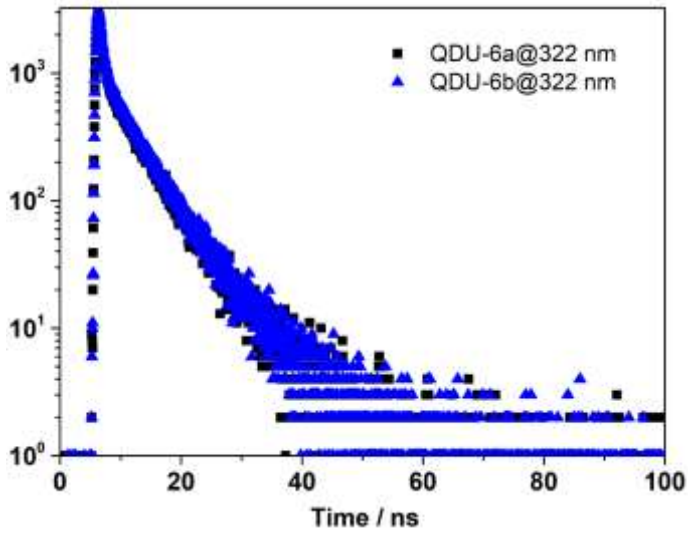

Fig. S3. PL decay spectra of QDU-6a and QDU-6b excited by a picosecond pulsed diode laser.

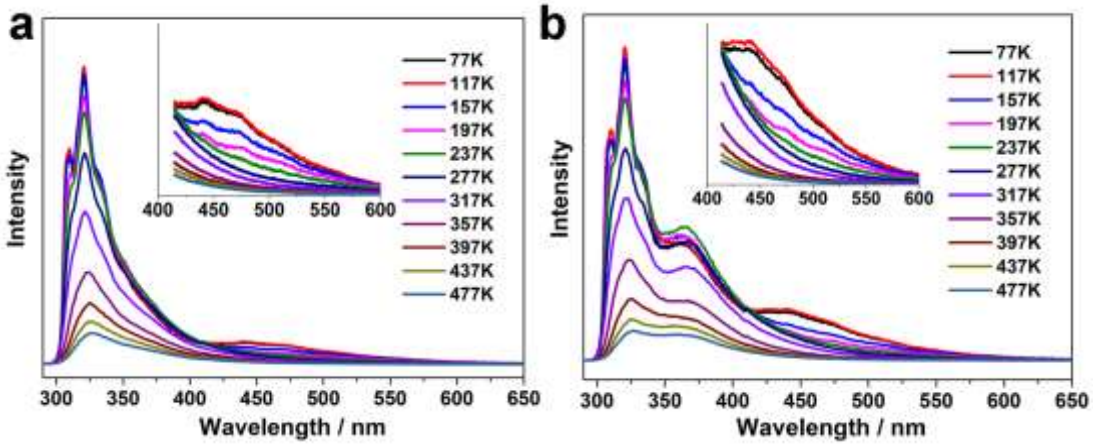

Fig. S4. Temperature-dependent luminescent emission spectra of (a) QDU-6a and (b) QDU-6b excited by 280 nm. The insets show the enlarge view of emission at about 450 nm.

Note: The emission spectra at around room temperature differ from those shown in Fig. 2. The prompt emission spectra were obtained by flashing xenon lamp with 0 ms delay and excitation at 310 nm. While the emission spectra at around room temperature in Fig. S4 were taken using a steady-state xenon lamp with excitation at 280 nm. Both the excitation light source and wavelengths may result in the different spectra in the two figures.

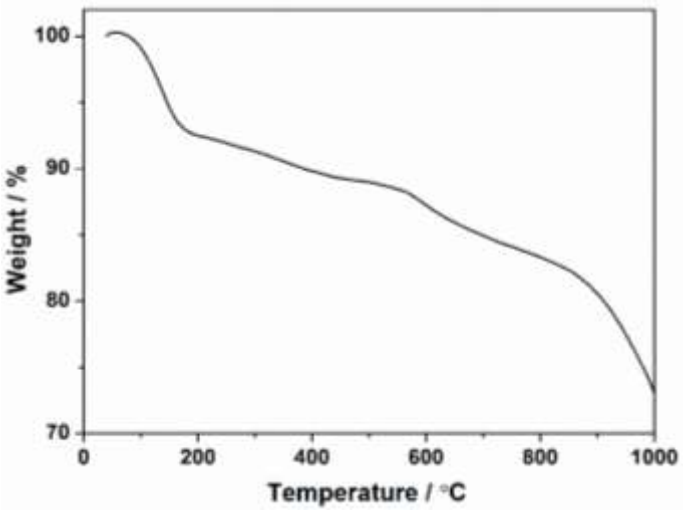

Fig. S5. Thermogravimetric analysis of compound QDU-6a.

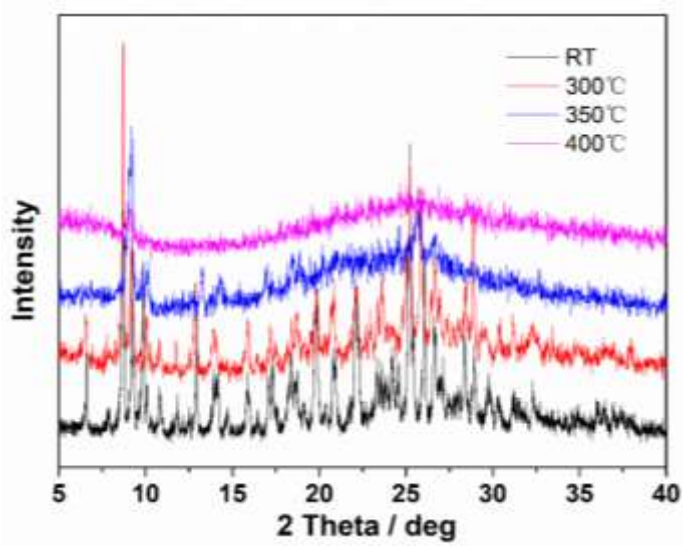

Fig. S6. PXRD patterns of QDU-6a and calcined samples at different temperatures as annotated.

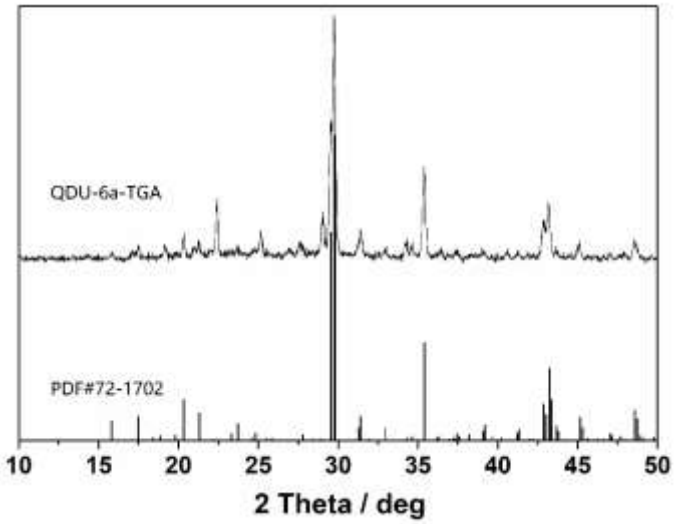

Fig. S7. PXRD patterns of the residue after TGA and zinc phosphate.

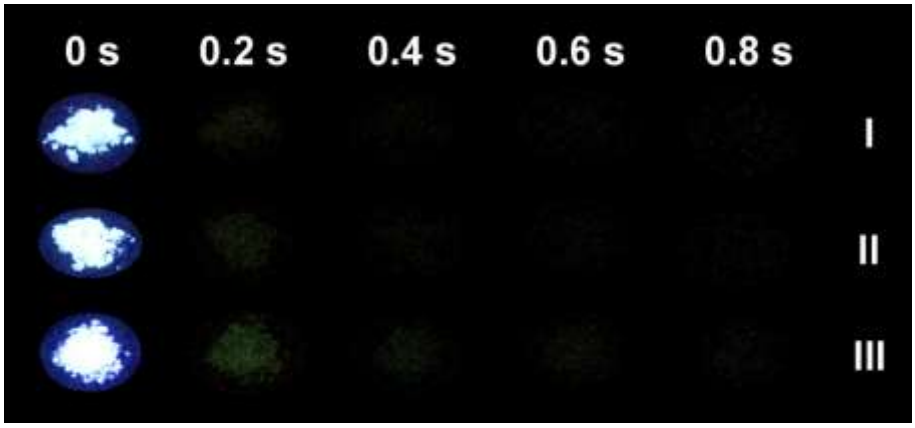

Fig. S8. Photographs of QDU-6b after heating at 300 °C for 30 min (I), grinding for 30 min (II) and placing in ethyl alcohol for 20 min (III).